

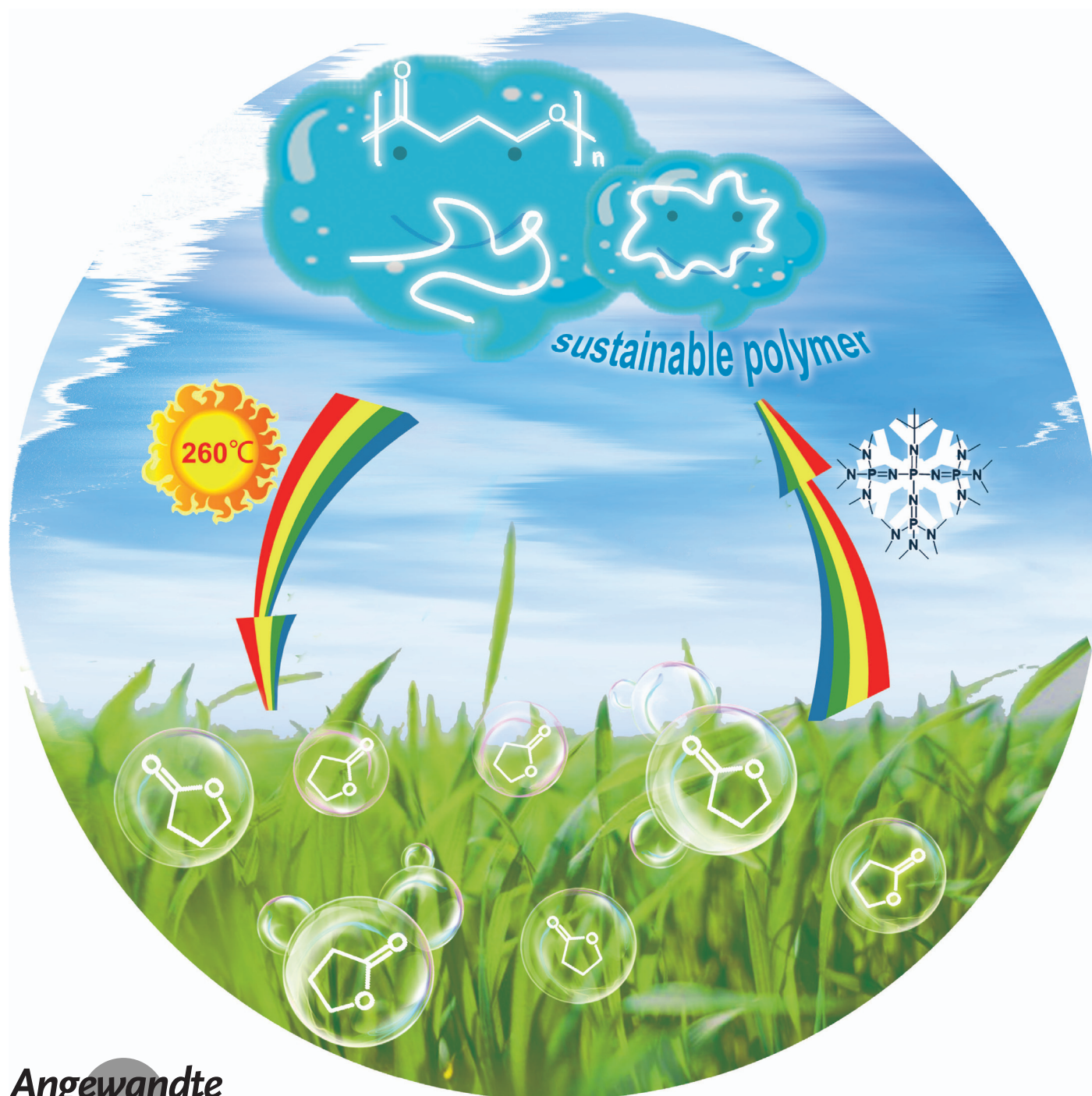


Sustainable Polymers Hot Paper

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Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester from Biorenewable Non-Strained γ -Butyrolactone

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Abstract: The first effective organopolymerization of the biorenewable “non-polymerizable” γ -butyrolactone (γ -BL) to a high-molecular-weight metal-free recyclable polyester is reported. The superbases *tert*-Bu-P₄ is found to directly initiate this polymerization through deprotonation of γ -BL to generate reactive enolate species. When combined with a suitable alcohol, the *tert*-Bu-P₄-based system rapidly converts γ -BL into polyesters with high monomer conversions (up to 90 %), high molecular weights (M_n up to 26.7 kg mol⁻¹), and complete recyclability (quantitative γ -BL recovery).

Organopolymerization^[1] using small-molecule organic compounds as catalysts or initiators has enabled the synthesis of a broad range of polymers through various mechanistic pathways and grown into a preferred method when metal-free products or processes are of primary concern. A class of organic catalysts that attracted increasing attention in polymer synthesis is polyaminophosphazenes,^[2] which are uncharged, extremely strong organic bases with low nucleophilicity. In particular, the P₄-phosphazene base, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylid-enamino]-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (*tert*-Bu-P₄), is one of the strongest known neutral bases with a pK_a of 30.2₅ (DMSO = dimethylsulfoxide) for its conjugate acid and the cation [*tert*-Bu-P₄H]⁺ being about 1.4 nm in diameter.^[3] Using its high Brønsted basicity, several effective metal-free initiator systems have been developed by combining *tert*-Bu-P₄ with a co-initiator such as an enolizable organic acid (to generate enolate active species) and alcohol (to generate alkoxide active species); examples highlighted here include anionic polymerization of methyl methacrylate (MMA),^[4] ring-opening polymerization (ROP) of cyclosiloxanes^[5] and ethylene oxide,^[6] as well as stereoselective ROP of lactide by the related 1-pyrene-butanol (PBNOL)/1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2 λ^5 ,4 λ^5 -catenadi(phosphazene) (*tert*-Bu-P₂) initiating system.^[7] *tert*-Bu-P₄ has also been employed as an efficient catalyst for the well-controlled group-transfer polymerization of MMA and other functionalized methacrylates initiated by a silyl ketene acetal.^[8]

We recently found that *tert*-Bu-P₄ can directly generate highly active species through its reaction with an appropriate monomer in the absence of any co-initiating component.^[9,10] For example, *tert*-Bu-P₄ brought about rapid polymerization of γ -methyl- α -methylene- γ -butyrolactone (γ -MMBL), proceeding through chain initiation that involves abstraction of an β -H of γ -MMBL by *tert*-Bu-P₄ to generate the highly reactive anionic monomer species [γ -MMBL^{-H}]⁻ and chain propagation that involves rapid conjugate addition of the resulting enolate anion stabilized by the nanosized cation [*tert*-Bu-P₄H]⁺ to monomer.^[9] A similar chain initiation pathway to generate an enolate species by deprotonation of

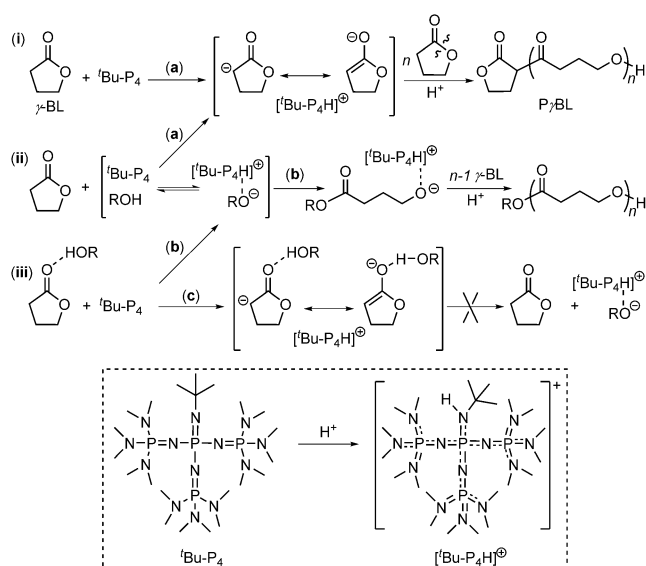
monomer was also recently reported in the ROP of lactide by a cyclopropenimine superbases.^[11]

Cyclic esters (lactones and lactides) with relatively high strain energy are desired building blocks for the construction of high-molecular-weight (high MW) aliphatic polyesters through the ROP process and a rapid chain-growth mechanism.^[12] The five-membered γ -butyrolactone (γ -BL) would also be a desirable bio-derived monomer for the chemical synthesis of biopolyester, poly(γ -butyrolactone) (P γ BL), as γ -BL is a key downstream chemical of succinic acid that was recently ranked first^[13] in the DOE's top 12 biomass-derived compounds^[14] best suited to replace petroleum-derived chemicals. However, it has been a challenge to convert the non-strained γ -BL, commonly referred as “non-polymerizable” in textbooks^[15] and literature,^[16] into high MW P γ BL, even under ultra-high pressure (e.g., 20000 atm)^[17] or lipase-catalyzed conditions.^[18] The non-polymerization or low oligomerization observed in the ROP of γ -BL under ambient pressure^[19] can be explained by its unfavorable thermodynamics because a large negative ΔS_p is not offset by a small change of ΔH_p of this ROP.^[20] On the other hand, high MW microbial poly(4-hydroxybutyrate) (P4HB),^[21] a structural equivalent of P γ BL, is produced through a bacterial fermentation process.^[22] Most recently, we discovered catalytic and thermodynamic conditions that enabled the first successful chemical ROP of γ -BL into high MW P γ BL with controlled linear or cyclic topologies and complete thermal recyclability, under readily accessible conditions (i.e., 1 atm, -40°C, THF).^[23] In that process, metal (La, Y)-catalyzed coordination ROP was found to be the most effective method to achieve high MW P γ BL (M_n up to 30 kg mol⁻¹) and high monomer conversion (up to 90 %). Considering the ROP of γ -BL to P γ BL as the chemical route to the biomaterial P4HB, it would be desirable that P γ BL could be produced by metal-free organopolymerization of γ -BL. However, commonly used organic catalysts highly effective for the ROP of typical cyclic esters, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), failed to produce high MW P γ BL, with $M_n \leq 6.2$ kg mol⁻¹ and yield ≤ 33 %.^[23] Table S1 in the Supporting Information summarizes the results of the ROP of γ -BL by five common organocatalysts, all of which produced low MW P γ BL with low yield. In short, the development of an effective organopolymerization of the non-strained γ -BL that exhibits good activity and can produce high MW polyester has remained elusive, which was the central goal of this study.

We hypothesized that the superbases *tert*-Bu-P₄ may promote rapid organopolymerization of γ -BL to high MW P γ BL through generation of highly active enolate anions by deprotonation of γ -BL using *tert*-Bu-P₄, followed by the ROP events [Scheme 1 (i)]. In fact, we showed experimentally and theoretically the feasibility for abstraction of the proton from α -C of γ -methyl- γ -butyrolactone (γ -valerolactone) by *tert*-Bu-P₄ to generate reactive enolate species.^[9] Guided by the above hypothesis and observation, we first examined the ROP of γ -BL using *tert*-Bu-P₄ alone (1.0 mol % loading) in toluene at -40°C. Indeed, the ROP proceeded appreciably, achieving 30.4 % conversion after 12 h and producing relatively high MW P γ BL with $M_n = 26.4$ kg mol⁻¹ and D (M_w/M_n) = 1.79 (run 1, Table 1). Increasing the base loading to 2.0 and

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Scheme 1. ROP of γ -BL via three different mixing procedures.

10 mol %, the polymerization achieved higher conversions of 38.3 and 59.0%, while the resulting $P\gamma$ BL had lower MWs with $M_n = 20.7$ ($\bar{D} = 1.63$, run 2) and 9.17 kg mol^{-1} ($\bar{D} = 1.16$, run 3), respectively. However, the polymerization was much more rapid and effective when *tert*-Bu- P_4 was premixed with BnOH, followed by addition of γ -BL. Thus, with a $[\gamma\text{-BL}]/[\text{tert-Bu-P}_4]/[\text{BnOH}]$ ratio of 100/1/1, the ROP under the same

conditions achieved 70% monomer conversion in 4 h (the reaction mixture gelled in 5 minutes), affording $P\gamma$ BL with $M_n = 26.7 \text{ kg mol}^{-1}$ and $\bar{D} = 2.01$ (run 4). Interestingly, when the ROP was started by adding *tert*-Bu- P_4 in toluene to a mixture of monomer and BnOH, the polymerization became much slower (34.7% conversion in 12 h) but more controlled, producing $P\gamma$ BL with a lower M_n of 18.7 kg mol^{-1} and a narrower $\bar{D}$ of 1.37 (run 5).

The above intriguing findings from the above three different ROP procedures were further examined collaboratively through analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) and NMR methods, and we subsequently explained the results with different initiating/propagating pathways. In the first procedure of the ROP by *tert*-Bu- P_4 alone, the MS spectrum (Figure 1) of the resulting $P\gamma$ BL consists of two series of molecular ion peaks, with the lower MW series A tentatively assigning to the cyclic $P\gamma$ BL with no chain ends [$M_{\text{end}} = 0 + 23(\text{Na}^+) \text{ g mol}^{-1}$] and the higher MW series B to the linear $P\gamma$ BL with acylated lactone/H chain ends [$M_{\text{end}} = 86.03 + 23(\text{Na}^+) \text{ g mol}^{-1}$]. Consistent with this bimodal MS distribution, the thermal gravimetric analysis (TGA) curve of this polymer (Figure S2) also showed two compositions, with the cyclic structure (the more thermally stable component^[23]) being the minor component. Furthermore, the acylated lactone/H chain ends were confirmed by ^1H and ^{13}C NMR spectra (Figures S3a and S4), as evidenced by the resonances at δ 4.24–4.40 [$-\text{CH}_2-\text{OC}(\text{O})-$], 3.07–3.16 [$-\text{C}(\text{O})-\text{CH}-$] and 2.65 ppm [$-\text{CH}_2-\text{CH}_2-\text{OC}(\text{O})-$] in ^1H NMR and the resonan-

Table 1: Results of ROP of γ -BL by Base/Alcohol Systems (TOL = toluene; THF = tetrahydrofuran; DMF = dimethylformamide).^[a]

Run	Base (B)	Initiator (I)	M/B/I ratio	T [°C]	Solvent	t [h]	Conv. ^[b] [%]	M_n ^[c] [kg mol ⁻¹]	$\bar{D}$ ^[c] (M_w/M_n)
1	<i>tert</i> -Bu- P_4	–	100/1/0	–40	TOL	12	30.4	26.4	1.79
2	<i>tert</i> -Bu- P_4	–	50/1/0	–40	TOL	12	38.3	20.7	1.63
3	<i>tert</i> -Bu- P_4	–	10/1/0	–40	TOL	12	59.0	9.17	1.16
4	<i>tert</i> -Bu- P_4	BnOH	100/1/1	–40	TOL	4	70.0	26.7	2.01
5 ^[d]	<i>tert</i> -Bu- P_4	BnOH	100/1/1	–40	TOL	12	34.7	18.7	1.37
6	<i>tert</i> -Bu- P_4	BnOH	100/1/1	–40	THF	4	81.0	26.2	2.05
7	<i>tert</i> -Bu- P_4	BnOH	100/1/1	–40	DMF	4	56.0	22.1	1.71
8	<i>tert</i> -Bu- P_4	BnOH	100/1/1	–28	THF	12	20.0	9.11	1.41
9	<i>tert</i> -Bu- P_4	BnOH	100/1/1	0	THF	12	2.24	n.d.	n.d.
10	<i>tert</i> -Bu- P_4	BnOH	100/1/1	25	THF	12	0	–	–
11	<i>tert</i> -Bu- P_4	BnOH	100/1/0.5	–40	THF	12	52.4	27.1	2.11
12	<i>tert</i> -Bu- P_4	BnOH	100/1/1.5	–40	THF	4	90.0	25.0	2.04
13	<i>tert</i> -Bu- P_4	BnOH	200/1/1	–40	THF	12	56.0	18.2	1.62
14	<i>tert</i> -Bu- P_4	Ph ₂ CHOH	100/1/1	–40	THF	4	85.0	23.2	1.97
15	<i>tert</i> -Bu- P_4	<i>i</i> PrOH	100/1/1	–40	THF	4	82.7	22.9	2.06
16	<i>tert</i> -Bu- P_4	PBNOL	100/1/1	–40	THF	4	77.9	21.5	1.97
17	<i>tert</i> -Bu- P_4	<i>tert</i> -BuOH	100/1/1	–40	THF	4	60.0	18.0	1.81
18	<i>tert</i> -Bu- P_2	BnOH	100/1/1	–40	THF	4	45.1	15.0	1.34
19	<i>tert</i> -Bu- P_2	Ph ₂ CHOH	100/1/1	–40	THF	4	48.4	12.2	1.30
20	<i>tert</i> -Bu- P_1	Ph ₂ CHOH	100/1/1	–40	THF	4	0	–	–
21	<i>tert</i> -BuOK	–	100/1	–40	THF	4	55.4	26.1	2.00
22	<i>tert</i> -BuOK	BnOH	100/1/1	–40	THF	4	74.5	17.7	1.54
23	NaOMe	–	100/1	–40	THF	4	12.6	19.8	1.51
24	NaOMe	BnOH	100/1/1	–40	THF	4	72.8	14.7	1.53
25	KH	–	100/1	–40	THF	4	13.9	36.8	1.82
26	KH	BnOH	100/1/1	–40	THF	4	73.3	21.7	1.71

[a] Conditions: $[\gamma\text{-BL}] = 10 \text{ M}$ (0.42 g, 4.9 mmol); base and initiator were mixed first, followed by γ -BL; n.d. = not determined. [b] Monomer conversion measured by ^1H NMR. [c] M_n and $\bar{D}$ were determined by GPC at 40 °C in DMF relative to PMMA standards. [d] BnOH initiator and γ -BL were mixed first, followed by addition of base.

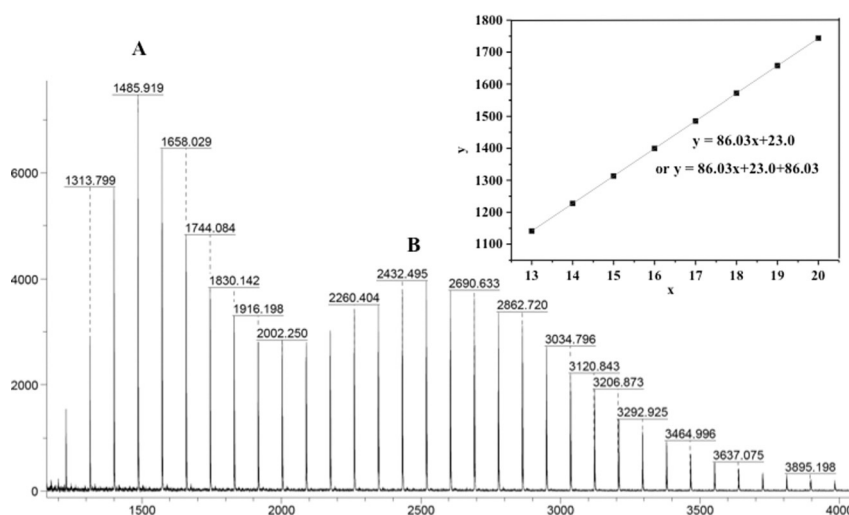


Figure 1. MALDI-TOF mass spectrum of P γ BL produced directly by *tert*-Bu-P₄ ($x = m/z$, $y = \text{intensity}$). Inset: plot of m/z values (y) versus the number of γ -BL repeat units (x).

ces at δ 194.26 (C=O), 67.46 [-CH₂-OC(O)-], 52.33 [-C(O)-CH<] and 30.87 ppm [-CH₂-CH₂-OC(O)-] in the ¹³C NMR spectrum. These results are consistent with the mechanistic scenario (a) outlined in Scheme 1 (i) involving deprotonation of γ -BL by *tert*-Bu-P₄ to generate the reactive lactone enolate anion that initiates the rapid polymerization. Noteworthy is that the signals corresponding to the C=C double bond were absent in ¹³C NMR, indicating that initiation involves the nucleophilic attack by the C-bonded enolate rather than the O-bonded enolate.

The ability of *tert*-Bu-P₄ to abstract α -H of γ -BL was also demonstrated by NMR studies of stoichiometric reactions. In a 1:1 ratio reaction in [D₈]toluene at room temperature (RT; under which conditions no polymerization took place), ¹H NMR spectrum taken after 10 minutes (Figure S5) showed that all γ -BL was consumed but not all *tert*-Bu-P₄ (δ 2.68 and 1.68 ppm in ¹H NMR; δ 4.84 and -25.34 ppm in ³¹P NMR, Figure S7b). The formation of [*tert*-Bu-P₄H]⁺ was confirmed via signals at δ 8.14–8.40, 2.56 and 1.50 ppm in ¹H NMR and δ 12.46 and -23.84 ppm in ³¹P NMR (Figure S7b). Increasing the amount of γ -BL to 2.2 equiv fully consumed all *tert*-Bu-P₄ (Figures S7c and S9), suggesting that 1 equiv of *tert*-Bu-P₄ reacts with 2 equiv of γ -BL to form an ion pair. The anion showed a complex series of resonances in ¹H NMR ([D₈]toluene, Figures S5 & S9), which was further analyzed by ¹H-¹H COSY spectra (Figure S11). Overall, these results indicated that the direct reaction of γ -BL and *tert*-Bu-P₄ formed [*tert*-Bu-P₄H]⁺ paired with an anionic dimer which can exist in either the ring-retention or ring-opening form (Figure S9), the ratio of which can be varied with reaction conditions (substrate ratio and reaction time). The NMR spectra taken in [D₅]bromobenzene (Figures S6, S8, S10, and S12) are consistent with the above structural analysis.

The second procedure of the ROP started by adding γ -BL to a premixed solution of *tert*-Bu-P₄ and BnOH resulted in the enhanced rate of the polymerization over the system by using *tert*-Bu-P₄ alone. Monitoring the stoichiometric reaction

between BnOH and *tert*-Bu-P₄ at RT by ¹H NMR (Figures S14a and S15) clearly revealed formation of complex [*tert*-Bu-P₄H⁺...OBn⁻] which is weakly paired through H bonding, as evidenced by the disappearance of the signal of the PhCH₂OH proton at 1.26 ppm and other corresponding spectral changes (Figure S15); the signal of the [*tert*-Bu-P₄H]⁺ proton was not observed at RT because of fast proton exchange, but the resonance of this proton at 13.9 ppm was observed at -60°C (Figure S16). The MS spectrum (Figure S17) of the P γ BL produced by this procedure exhibited two series of molecular ion peaks, corresponding to P γ BL with acylated lactone/H chain ends (A series) and BnO/H chain ends (B series); the presence of such chain ends was also confirmed by ¹H NMR, showing a 1:1 ratio of the two types of the chain

ends (Figure S3b). Overall, these results are consistent with the mechanistic scenario outlined in Scheme 1 (ii), involving initiation pathways via both the BnO⁻ anion (pathway b) and the enolate anion (pathway a) formed through deprotonation of BnOH and γ -BL by *tert*-Bu-P₄, respectively. This dual initiation gave faster rates of polymerization but also led to P γ BL with a broader molecular weight distribution ($\bar{D} = 2.01$).

The third procedure of the polymerization started by adding *tert*-Bu-P₄ to the mixture of γ -BL and BnOH led to the decreased activity but increased control. The stoichiometric reaction between γ -BL and BnOH revealed weak activation of BnOH by γ -BL through hydrogen bonding (Figure S18). The MS spectrum of the P γ BL obtained using this procedure (Figure S19) also showed two series of molecular ion peaks attributed to acylated lactone/H and BnO/H chain ends, with the estimated ratio of acylated lactone/BnO = 15/85 by ¹H NMR (Figure S3c). Overall, these results are consistent with the mechanistic scenario outlined in Scheme 1 (iii), involving also two initiation pathways via the BnO⁻ anion (pathway b) and the enolate anion (pathway a). However, this procedure apparently preferred pathway b over a, thus producing P γ BL with predominant BnO/H chain ends. In addition, pathway b involves the stabilized propagating alkoxide chain ends via H-bonding, thus accounting for the observed more controlled polymerization. The reduced activity is presumably due to the presence of non-productive pathway c, namely (i) + ROH, as we observed that the system became inactive when BnOH was added to the premixed solution of *tert*-Bu-P₄ and γ -BL (pathway a).

Fixing the ROP procedure to Scheme 1 (ii), which was the most rapid polymerization system and also produced P γ BL with the highest MW, we further explored this ROP under different reaction conditions, initiators and bases. First, changing the solvent from the relative nonpolar toluene to polar dichloromethane (DCM) resulted in no monomer conversion because of rapid decomposition of *tert*-Bu-P₄ in this solvent (dissolving *tert*-Bu-P₄ in DCM resulted in a brown

solution). On the other hand, performing the polymerization in THF enhanced the conversion to 81.0% (run 6) from 70.0% in toluene while the MW remained high ($M_n = 26.2 \text{ kg mol}^{-1}$). However, using the more polar *N,N*-dimethylformamide (DMF) decreased the activity achieving only modest conversion of 56.0% (run 7). Kinetic profiling of the ROP at -40°C in THF revealed that the ROP proceeded rapidly in the beginning and conversion up to 70.7% was achieved in only 11 minutes (Figure S20), after which time the ROP went slowly and achieved only additional 10% of monomer conversion in next 4 h. However, a gradual increase in MW of the resulting polymers was observed. Second, elevating the temperature from -40°C to -28°C , the conversion decreased drastically from 81.0% to 20.0% (run 8), and the conversion was only 2.24% for the polymerization at 0°C (run 9) and no polymerization was observed at 25°C (run 10). Third, increasing the amount of BnOH from 0.5 to 1.0 to 1.5 equiv relative to *tert*-Bu-P₄, the conversion enhanced significantly from 52.4% (12 h, run 11) to 81.0% (4 h, run 6) to 90.0% (4 h, run 12) with only a little change in polymer MW ($M_n = 25.0\text{--}27.1 \text{ kg mol}^{-1}$). On the other hand, increasing the $[\gamma\text{-BL}]/[\text{BnOH}]$ ratio from 100/1 to 200/1 led to a decrease in MW from 26.2 to 14.4 kg mol^{-1} (run 13), caused presumably by chain transfer to monomer. Fourth, screening the alcohols having different steric bulk and acidity included BnOH, Ph₂CHOH, *i*PrOH, PBNOL, and *tert*-BuOH. Under the same conditions, the γ -BL conversion was found to increase in the following order: *tert*-BuOH < PBNOL < BnOH < *i*PrOH < Ph₂CHOH (runs 6, 14–17), which apparently correlates with the steric bulk and acidity of alcohol and the nucleophilicity of the alkoxy anion. Fifth, under the same conditions for the base/ROH system, the weaker base *tert*-Bu-P₂ (the basicity of which is not high enough to deprotonate γ -BL, Figure S22) reduced the conversion by about one half (runs 18 and 19) compared with that by *tert*-Bu-P₄, while no activity was observed when the weakest base of the series, *tert*-Bu-P₁, was employed (run 20). These results showed that the ROP activity decreases with decreasing the basicity of the superbases, which correlates well with the degree of alcohol activation as revealed by NMR analysis (Figures S15, S23, and S24).

As a comparative study, we also investigated the performance of some common inorganic bases including *tert*-BuOK, NaOMe and KH. Overall, the polymerizations by such bases were less active than that by *tert*-Bu-P₄, either using alone or in combination with BnOH (runs 21–26), although in some cases comparable ($M_n = 26.1 \text{ kg mol}^{-1}$ by *tert*-BuOK) or even higher ($M_n = 36.8 \text{ kg mol}^{-1}$ by KH) MW polymers can be achieved. Investigations by MS (Figures S25 and S26) and NMR (Figures S27 and S28) also indicated that the initiation pathways through monomer deprotonation and alcohol activation by the base are similar to those already demonstrated by *tert*-Bu-P₄.

In conclusion, we have developed the first effective organopolymerization of the bio-derived non-strained five-membered lactone γ -BL for the synthesis of high MW, metal-free polyester P γ BL. As the P γ BL produced by the metal-mediated coordination ROP, the P γ BL obtained by the current organopolymerization is completely recyclable back

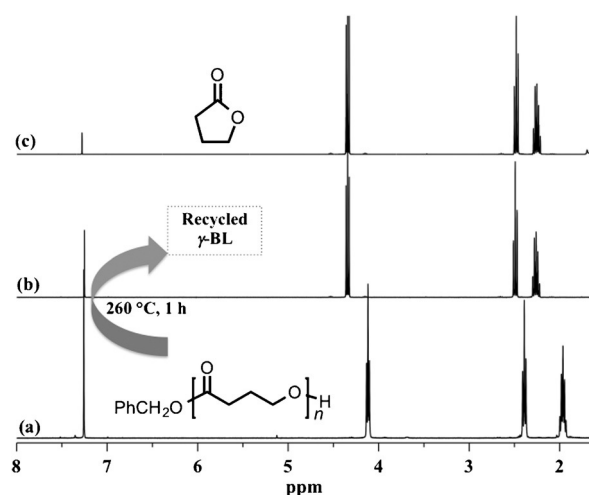


Figure 2. ^1H NMR spectra (CDCl_3 , 25°C): a) P γ BL ($M_n = 26.7 \text{ kg mol}^{-1}$, prepared by *tert*-Bu-P₄/BnOH); b) the liquid product obtained after heating P γ BL at 260°C for 1 h; c) γ -BL monomer for comparison.

to its monomer in the pure state upon heating the bulk polymer at 260°C for 1 h (Figure 2, and Figures S35–S37). The BnO/H end groups also reform back to the starting initiator BnOH after thermal recycling (Figures S38 and S39). The superbases *tert*-Bu-P₄ can directly initiate this challenging ROP through deprotonation of γ -BL to generate the reactive enolate species. However, an even more effective ROP system is based on the H-bonding paired complex [*tert*-Bu-P₄H⁺...OBn[−]], formed via mixing of *tert*-Bu-P₄ with ROH; this system enabled high monomer conversions (up to 90%) and high MW polymers (M_n up to 26.7 kg mol^{-1}) in a relatively short time period (4 h or less). Investigations into the effects of reaction conditions as well as structures of alcohol initiators and organic base catalysts have identified the currently most effective organic initiator and catalyst for this ROP to be BnOH or Ph₂CHOH and *tert*-Bu-P₄ superbases, respectively. An understanding of mechanistic scenarios of this organopolymerization has also led to the effective ROP system based on simple inorganic bases such as *tert*-BuOK/BnOH and KH/BnOH. Overall, the results reported herein established P γ BL as a truly sustainable polymer: it is biorenewable, organically synthesized, and completely recyclable.

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Keywords: organopolymerization · polyesters · recyclability · superbases · sustainable polymers

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- [1] Selected reviews on organopolymerization: a) S. Naumann, A. P. Dove, *Polym. Chem.* **2015**, *6*, 3185–3200; b) S.-I. Matsuoka, *Polym. J.* **2015**, *47*, 713–718; c) H. Sardon, A. Pascual, D.

- Mecerreyes, D. Taton, H. Cramail, J. L. Hedrick, *Macromolecules* **2015**, *48*, 3153–3165; d) J. Zhao, N. Hadjichristidis, Y. Gnanou, *Polimery* **2014**, *59*, 49–59; e) C. Thomas, B. Bibal, *Green Chem.* **2014**, *16*, 1687–1699; f) S. Naumanna, M. R. Buchmeiser, *Catal. Sci. Technol.* **2014**, *4*, 2466–2479; g) L. Mespouille, O. Coulembier, M. Kawalec, A. P. Dove, P. Dubois, *Prog. Polym. Sci.* **2014**, *39*, 1144–1164; h) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* **2013**, *42*, 2142–2172; i) H. A. Brown, R. M. Waymouth, *Acc. Chem. Res.* **2013**, *46*, 2585–2596; j) K. Fuchise, Y. Chen, T. Satoh, T. Kakuchi, *Polym. Chem.* **2013**, *4*, 4278–4291; k) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2010**, *43*, 2093–2107; l) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* **2007**, *107*, 5813–5840.
- [2] a) R. Schwesinger, H. Schlemper, C. Hasenfratz, J. Willaredt, T. Dambacher, T. Breuer, C. Ottaway, M. Fletschinger, J. Boele, *Liebigs Ann.* **1996**, 1055–1081; b) R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E. M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1361–1363; *Angew. Chem.* **1993**, *105*, 1420–1422; c) R. Schwesinger, H. Schlemper, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167–1169; *Angew. Chem.* **1987**, *99*, 1212–1214; d) R. Schwesinger, *Chimia* **1985**, *39*, 269–272.
- [3] I. Leito, T. Rodima, I. A. Koppel, R. Schwesinger, V. M. Vlasov, *J. Org. Chem.* **1997**, *62*, 8479–8483.
- [4] T. Pietzonka, D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 716–717; *Angew. Chem.* **1993**, *105*, 741–742.
- [5] A. Molenberg, M. Möller, *Macromol. Rapid Commun.* **1995**, *16*, 449–453.
- [6] a) B. Esswein, M. Möller, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 623–625; *Angew. Chem.* **1996**, *108*, 703–705; b) B. Eßwein, N. M. Steidl, M. Möller, *Macromol. Rapid Commun.* **1996**, *17*, 143–148.
- [7] L. Zhang, F. Nederberg, J. M. Messman, R. C. Pratt, J. L. Hedrick, C. G. Wade, *J. Am. Chem. Soc.* **2007**, *129*, 12610–12611.
- [8] a) S. Kikuchi, Y. Chen, K. Fuchise, K. Takada, J. Kitakado, S.-I. Sato, T. Satoh, T. Kakuchi, *Polym. Chem.* **2014**, *5*, 4701–4709; b) Y. Chen, K. Fuchise, A. Narumi, S. Kawaguchi, T. Satoh, T. Kakuchi, *Macromolecules* **2011**, *44*, 9091–9098; c) J.-C. Hsu, Y. Chen, T. Kakuchi, W.-C. Chen, *Macromolecules* **2011**, *44*, 5168–5177; d) T. Kakuchi, Y. Chen, J. Kitakado, K. Mori, K. Fuchise, T. Satoh, *Macromolecules* **2011**, *44*, 4641–4647.
- [9] M. Schmitt, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *Polym. Chem.* **2014**, *5*, 3261–3270.
- [10] a) S. Feng, M. Schmitt, E. Y.-X. Chen, *Macromol. Chem. Phys.* **2015**, *216*, 1421–1430; b) J. Tang, E. Y.-X. Chen, *Org. Chem. Front.* **2015**, *2*, 1625–1631.
- [11] T. S. Stukenbroeker, J. S. Bandar, X. Zhang, T. H. Lambert, R. M. Waymouth, *ACS Macro Lett.* **2015**, *4*, 853–856.
- [12] Selected recent reviews: a) J.-F. Carpentier, *Organometallics* **2015**, *34*, 4175–4189; b) M. A. Hillmyer, W. B. Tolman, *Acc. Chem. Res.* **2014**, *47*, 2390–2396; c) A. Sauer, A. Kapelski, C. Flidel, S. Dagorne, M. Kol, J. Okuda, *Dalton Trans.* **2013**, *42*, 9007–9023; d) C. Jérôme, P. Lecomte, *Adv. Polym. Sci.* **2012**, *245*, 173–217; e) A.-C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466–1486; f) A.-C. Albertsson, I. K. Varma, *Adv. Polym. Sci.* **2002**, *157*, 1–40; g) B. J. O’Keefe, M. A. Hillmyer, W. B. Tolman, *Dalton Trans.* **2001**, 2215–2224.
- [13] M. M. Bomgardner, *Chem. Eng. News* **2014**, *92*, 10–14.
- [14] a) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539–554; b) *Top value added chemicals from biomass* (Eds.: T. Werpy, G. R. Petersen), U.S. Department of Energy report: DOE/GO-102004-101992, **2004**.
- [15] a) H. R. Allcock, F. W. Lampe, J. E. Mark, *Contemporary Polymer Chemistry*, Pearson Education Inc., Upper Saddle River, 3rd ed., **2003**, p. 155; b) G. Odian, *Principles of Polymerization*, Wiley-Interscience, New York, 3rd ed., **1991**, p. 570; c) H. Sawada, *Thermodynamics of Polymerization*, Marcel Dekker, New York, **1976**, p. 150.
- [16] K. H. Houk, A. Jabbari, H. K. Hall, Jr., C. Alemán, *J. Org. Chem.* **2008**, *73*, 2674–2678.
- [17] a) K. Yamashita, K. Yamamoto, J.-I. Kadokawa, *Chem. Lett.* **2014**, *43*, 213–215; b) A. Oishi, Y. Taguchi, K. Fujita, *Jpn. Pat. JP2003252968*, **2003**; c) A. Oishi, Y. Taguchi, K. Fujita, Y. Ikeda, T. Masuda, *Jpn. Pat. JP2000281767*, **2000**; d) F. Korte, W. Glet, *J. Polym. Sci. Part B* **1966**, *4*, 685–689.
- [18] G. A. R. Nobes, R. J. Kazlauskas, R. H. Marchessault, *Macromolecules* **1996**, *29*, 4829–4833.
- [19] a) A. Duda, S. Penczek, *Macromol. Chem. Phys.* **1996**, *197*, 1273–1283; b) A. Duda, T. Biela, J. Libiszowski, S. Penczek, P. Dubois, D. Mecerreyes, R. Jérôme, *Polym. Degrad. Stab.* **1998**, *59*, 215–222.
- [20] a) “Thermodynamics and kinetics of ring-opening polymerization”: A. Duda, A. Kowalski in *Handbook of Ring-Opening Polymerization* (Eds.: P. Dubois, O. Coulembier, J.-M. Raquez), Wiley-VCH, Weinheim, **2009**, chap. 3; b) C. Alemán, O. Betran, J. Casanovas, K. H. Houk, H. K. Hall, Jr., *J. Org. Chem.* **2009**, *74*, 6237–6244; c) W. Saiyasombat, R. Molloy, T. M. Nicholson, A. F. Johnson, I. M. Ward, S. Poshychinda, *Polymer* **1998**, *39*, 5581–5585.
- [21] T. Moore, R. Adhikari, P. Gunatillake, *Biomaterials* **2005**, *26*, 3771–3782.
- [22] D. P. Martin, S. F. Williams, *Biochem. Eng. J.* **2003**, *16*, 97–105.
- [23] M. Hong, E. Y.-X. Chen, *Nat. Chem.* **2016**, *8*, 42–49.

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